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PVP-SO₂ complex as a solid mild acid catalyst for efficient one pot, three component, Strecker synthesis of α -aminonitriles

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Solid poly(4-vinylpyridine)-SO₂ complex was prepared and used as a mild solid acid catalyst for simple and efficient three component Strecker synthesis of α -aminonitriles in high yield and purity.

KEY WORDS: PVP-SO₂ complex; solid support; Strecker reaction; α-aminonitriles.

1. Introduction

Polymer supported reagents are becoming important and useful tools in synthetic organic chemistry [1]. The solid support, not only makes the reactions simple, easy and environmentally safer, but also helps sometimes to fine-tune the reactivity of the reagents towards various synthetic transformations. Recently, we were interested in using poly(4-vinylpridine) (PVP) as a solid support for various acidic gaseous and liquid reagents and catalysts. During the course of our studies, we found that solid PVP and SO₂ gas form a stable, solid 1:1 complex (one SO₂ per one pyridine unit), which can be used as a solid supported SO₂ equivalent.

Strecker reaction [2] is a useful way to synthesize bilogically important α-aminonitriles, which has been extensively studied using a variety of catalysts such as metal triflates, NiCl₂, BiCl₃, ZnX₂, RuCl₃, LiClO₄, etc [3]. Majority of these reactions involve the use of expensive reagents and catalysts, harsher reaction conditions, longer reaction time and tedious work up or purification methods to afford the α -aminonitriles in analytically pure form. Recently, Strecker reaction using solid supported catalysts has drawn significant attention [4]. Realizing the importance of the Strecker reaction and the role of a solid catalyst in organic synthesis, we decided to explore the potential use of the solid PVP-SO₂ complex as a mild acidic catalyst in the reaction. Herein, we disclose our studies on PVP-SO₂ complex and its use as an effecient catalyst in one pot, three component, Strecker reaction for the synthesis of α -aminonitriles.

2. Experimental

All chemicals were purchased from commercial sources and were used as such. PVP-SO₂ complex was

*To whom correspondence should be addressed. E-mail: olah@usc.edu prepared by following the procedure described below. 1 H, 13 C and 19 F NMR spectra were recorded on Varian NMR spectrometers at 400 MHz and 300 MHz, respectively. 1 H NMR chemical shifts were determined relative to internal tetramethylsilane at δ 0.0 ppm. 13 C NMR chemical shifts were determined relative to internal tetramethylsilane at δ 0.0 ppm or to the 13 C signal of CDCl₃ at δ 77.0 ppm. 19 F NMR chemical shifts were determined relative to internal CFCl₃ at δ 0.0 ppm.

2.1. Preparation of the PVP-SO₂ complex

In a Nalgene bottle, 2% cross-linked poly(4-vinyl-pyridine) was taken and the container was cooled to – 78 °C under dry nitrogen atmosphere. Keeping the temperature constant, SO₂ gas was passed slowly through the polymer with vigorous shaking of the mixture. The morphology of the complex changed during the course of the addition and formed a bright yellow fine powder. The addition of SO₂ was continued till the molar ratio of poly(4-vinyl pyridine) to SO₂ reached 1:1. Any excess amount of SO₂ could be removed by warming the powder to room temperature. The complex was stored cold (–20 °C) under dry conditions.

2.2. One pot synthesis of α -aminonitriles

To a solution of the aldehyde (1 mmol) and the amine (1 mmol) in dichloromethane (4 mL) taken in pressure tube, PVP-SO₂ complex (0.1 g) was added followed by TMSCN (2 mmol) and sealed. The mixture was stirred under heating at 50 °C for the specified amount of time. Progress of the reaction was monitored by NMR and TLC at different time intervals. After completion of the reaction, the mixture was filtered and the residue was washed several times with dichloromethane. The solvent from the collected filtrate was then removed under reduced pressure to get the crude product. Further purification was carried out by tituration of the products with excess hexanes and removal of the hexanes under

reduced pressure. This process was repeated several times till the product achieved desired purity. All the products were characterized by analyzing their spectral data (¹H, ¹³C, ¹⁹F). The residue (PVP) left after washing and filtration was dried and recycled for further complexation with SO₂.

2.3. NMR data of the α -aminonitrile compounds

2.3.1. 2-Phenyl-2-(phenylamino) acetonitrile (Table 1, entry 1)

¹H NMR: δ 4.12 (brs, 1H), 5.42 (s, 1H), 6.77 (d, J = 7.69 Hz, 2H), 6.90 (t, J = 7.41 Hz, 1H), 7.24–7.29 (m, 2H), 7.40–7.46 (m, 3H), 7.58–7.60 (m, 2H); ¹³C NMR: δ 50.1, 114.1, 118.2, 120.2, 127.2, 129.3, 129.50, 129.53, 133.9, 144.6

2.3.2. 2-(4-Fluorophenyl)-2-(phenylamino)acetonitrile (Table 1, entry 2)

¹H NMR: δ 4.03 (brs, 1H), 5.41 (s, 1H), 6.76 (d, J = 7.69 Hz, 2H), 6.90 (t, J = 7.51 Hz, 1H), 7.11–7.16 (m, 2H), 7.24–7.30 (m, 2H), 7.56–7.60 (m, 2H); ¹³C NMR: δ 49.5, 114.2, 116.3 (d, $^2J_{C-F} = 22.13$ Hz),118.0, 120.4, 129.1 (d, $^3J_{C-F} = 9.16$ Hz), 129.6, 129.7 (d, $^4J_{C-F} = 3.05$ Hz), 144.4, 163.2 (d, $^1J_{C-F} = 249.48$ Hz); 19F NMR: δ –112.0 (m).

2.3.3. 2-(4-Bromophenyl)-2-(phenylamino)acetonitrile (Table 1, entry 3)

¹H NMR: δ 4.03 (brs, 1H), 5.38 (s, 1H), 6.73 (d, J = 7.69 Hz, 2H), 6.90 (t, J = 7.41 Hz, 1H), 7.23–7.28 (m, 2H), 7. 46 (d, J = 8.0 Hz, 2H), 7. 57 (d, J = 8.61 Hz, 2H); ¹³C NMR: δ 49.7, 114.3, 117.7, 120.6, 123.7, 128.83, 129.6, 132.5, 132.9, 144.3.

2.3.4. 2-(4-Methoxyphenyl)-2-(phenylamino)acetonitrile (Table 1, entry 4)

¹H NMR: δ 3.84 (s, 3H), 4.0 (brs, 1H), 5.36 (s, 1H), 6.77 (d, J = 8.61 Hz, 2H), 6.89 (t, J = 7.42 Hz, 1H), 6.96 (d, J = 8.79 Hz, 2H), 7.25–7.30 (m, 2H), 7.51 (d, J = 8.69 Hz, 2H); ¹³C NMR: δ 49.6, 55.4, 114.1, 114.6, 118.4, 120.2, 125.9, 128.6, 129.5, 144.7, 160.4.

2.3.5. 2-(2-Methylphenyl)-2-(phenylamino)acetonitrile (Table 1, entry 5)

¹H NMR: δ 2.36 (s, 3H), 3.80 (brs, 1H), 5.45 (s, 1H), 6.77 (d, J = 8.97 Hz, 2H), 6.89 (t, J = 7.41 Hz, 1H), 7.23–7.34 (m, 5H), 7.69 (dd, J = 7.32 Hz, J = 1.83 Hz, 1H); ¹³C NMR: δ 18.6, 48.0, 113.8, 118.3, 120.1, 126.9, 127.5, 129.6, 129.7, 131.3, 132.0, 136.5, 144.8.

2.3.6. 2-(4-Ethylphenyl)-2-(phenylamino)acetonitrile (Table 1, entry 6)

¹H NMR: δ 1.23 (t, J = 7.69 Hz, 3H), 2.65 (q, J = 7.69 Hz, 2H), 4.08 (brs, 1H), 5.33 (s, 1H), 6.74 (d, J = 7.69 Hz, 2H), 6.86 (t, J = 7.41 Hz, 1H), 7.21–7.25 (m, 4H), 7.46 (d, J = 8.06 Hz, 2H); ¹³C NMR: δ 15.4,

28.4, 49.8, 114.0, 118.3, 120.0, 127.2, 128.7, 129.4, 131.1, 144.7, 145.7.

2.3.7. 2-(Phenylamino)-2-(3-trifluoromethylphenyl) acetonitrile (Table 1, entry 7)

¹H NMR: δ 4.06 (d, J = 6.59 Hz, 1H), 5.49 (d, J = 6.23 Hz, 1H), 6.76 (d, J = 7.69 Hz, 2H), 6.91 (t, J = 7.41 Hz, 1H), 7.23–7.29 (m, 2H), 7.58 (t, J = 7.87 Hz, 1H), 7.69 (d, J = 7.87 Hz, 1H), 7.81 (d, J = 7.69 Hz, 1H), 7.86 (s, 1H); ¹³C NMR: δ 49.8, 114.3, 117.6, 120.7, 123.6 (q, ${}^{1}J_{C-F}$ = 273.14 Hz), 124.1 (q, ${}^{3}J_{C-F}$ = 3.81 Hz), 126.3 (q, ${}^{3}J_{C-F}$ = 3.81 Hz), 129.6, 129.9, 130.5, 131.3 (q, ${}^{2}J_{C-F}$ = 32.8 Hz), 134.9, 144.2; ¹⁹F NMR: δ –63.2.

2.3.8. 2-(9-Anthryl)-2-(phenylamino)acetonitrile (Table 1, entry 8)

¹H NMR: δ 4.29 (d, J = 4.21 Hz, 1H), 6.66 (d, J = 4.40 Hz, 1H), 6.93–6.97 (m, 3H), 7.33–7.37 (m, 2H), 7.52–7.56 (m, 2H), 7.61–7.66 (m, 2H), 8.11 (d, J = 8.42 Hz, 2H), 8.43 (d, J = 8.97 Hz, 2H), 8.60 (s, 1H); ¹³C NMR: δ 44.2, 113.5, 119.0, 120.0, 123.1, 123.9, 125.5, 127.8, 129.2, 129.69, 129.72, 130.6, 131.5, 145.3.

2.3.9. 2-(2-Naphthyl)-2-(phenylamino)acetonitrile (Table 1, entry 9)

¹H NMR: δ 4.10 (d, J = 6.05 Hz, 1H), 5.86 (d, J = 5.86 Hz, 1H), 6.79 (d, J = 8.51 Hz, 2H), 6.90 (t, J = 7.41, Hz, 1H), 7.25–7.30 (m, 2H), 7.53–7.56 (m, 2H), 7.59 (dd, J = 8.60 Hz, J = 1.83 Hz, 1H), 7.85–7.87 (m, 2H), 7.90 (d, J = 8.60 Hz, 1H), 8.10 (s, 1H); ¹³C NMR: δ 50.2, 114.1, 118.2, 120.2, 124.3, 126.5, 126.9, 127.1, 127.7, 128.2, 129.3, 129.5, 131.0, 133.0, 133.4, 144.6.

2.3.10. 4-Phenyl-2-phenylamino-but-3-enenitrile (Table 1, entry 10)

¹H NMR: δ 3.90 (brs, 1H), 5.05 (d, J = 4.03 Hz, 1H), 6.27 (dd, J = 15.93 Hz, J = 5.13 Hz, 1H), 6.77 (d, J = 8.51 Hz, 2H), 6.90 (t, J = 8.40 Hz, 1H), 7.04 (dd, J = 15.94 Hz, J = 1.47 Hz, 1H), 7.25–7.29 (m, 2H), 7.30–7.39 (m, 3H), 7.41–7.44 (m, 2H); ¹³C NMR: δ 47.7, 114.3, 117.7, 120.3, 120.9, 126.9, 128.8, 128.9, 129.6, 134.9, 135.1, 144.4.

2.3.11. 2-(4-Chlorophenyl)-2-(isopropylamino) acetonitrile (Table 2, entry 1)

¹H NMR: δ 1.12 (d, J = 6.41 Hz, 6H), 1.45 (brs, 1H), 3.19 (heptet, J = 6.23 Hz, 1H), 4.76 (s, 1H), 7.37 (d, J = 8.43 Hz, 2H), 7.47 (d, J = 8.42 Hz, 2H); ¹³C NMR: δ 21.3, 23.5, 47.2, 51.6, 118.7, 128.6, 129.1, 133.9, 134.9.

2.3.12. 2-(4-Chlorophenyl)-2-(cyclopentylamino) acetonitrile (Table 2, entry 2)

¹H NMR: δ 1.34–1.43 (m, 2H), 1.55–1.66 (m, 3H), 1.68–1.76 (m, 2H), 1.82–1.92 (m, 2H), 3.42 (quintet,

J = 6.23, 1H), 4.68 (s, 1H), 7.35 (d, J = 8.43 Hz, 2H), 7.45 (d, J = 8.42 Hz, 2H); ¹³C NMR: δ 23.75, 23.80, 32.1, 33.5, 52.6, 57.7, 118.9, 128.5, 128.9, 133.8, 134.6.

2.3.13. 2-(4-Chlorophenyl)-2-(benzylamino)acetonitrile (Table 2, entry 3)

¹H NMR: δ 1.89 (brs, 1H), 3.91 (d, J = 13.0 Hz, 1H), 4.01 (d, J = 13.0 Hz, 1H), 4.70 (s, 1H), 7.28–7.38 (m, 7H), 7.46 (d, J = 8.60 Hz, 2H); ¹³C NMR: δ 51.1, 52.7, 118.3, 127.7, 128.3, 128.6, 128.9, 129.1, 133.1, 134.9, 137.8.

2.3.14. 2-(4-Chlorophenyl)-2-(phenylamino)acetonitrile (Table 2, entry 4)

¹H NMR: δ 4.07 (s, 1H), 5.40 (s, 1H), 6.75 (d, J = 8.51 Hz, 2H), 6.90 (t, J = 7.41 Hz, 1H), 7.24–7.29 (m, 2H), 7.41 (d, J = 8.60 Hz, 2H), 7.52 (d, J = 8.42 Hz, 2H); ¹³C NMR: δ 49.5, 114.2, 117.8, 120.5, 128.5, 129.4, 129.60, 132.3, 135.5, 144.3.

2.3.15. 2-(4-Chlorophenyl)-2-(4-methylphenylamino) acetonitrile (Table 2, entry 5)

¹H NMR: δ 2.27 (s, 3H), 3.92 (d, J = 6.77 Hz, 1H), 5.37 (d, J = 7.87 Hz, 1H), 6.67 (d, J = 8.43 Hz, 2H), 7.07 (d, J = 8.42 Hz, 2H), 7.41 (d, J = 8.61 Hz, 2H), 7.52 (d, J = 8.24 Hz, 2H); ¹³C NMR: δ 20.5, 50.0, 114.6, 117.9, 128.5, 129.4, 129.98, 130.04, 132.5, 135.4, 142.0.

2.3.16. 2-(4-Chlorophenyl)-2-(4-methoxyphenylamino) acetonitrile (Table 2, entry 6)

¹H NMR: δ 3.75 (s, 3H), 3.83 (brs, 1H), 5.31 (s, 1H), 6.73 (d, J = 8.97 Hz, 2H), 6.83 (d, J = 8.97 Hz, 2H), 7.40 (d, J = 8.61 Hz, 2H), 7.52 (d, J = 8.42 Hz, 2H); ¹³C NMR: δ 50.9, 55.6, 114.9, 116.5, 118.1, 128.5, 129.4, 132.5, 135.4, 138.1, 154.2.

2.3.17. 2-(4-Chlorophenyl)-2-(4-fluorophenylamino) acetonitrile (Table 2, entry 7)

¹H NMR: δ 3.98 (d, J = 8.24 Hz, 1H), 5.31 (d, J = 8.24 Hz, 1H), 6.69–6.73 (m, 2H), 6.95–7.0 (m, 2H), 7.42 (d, J = 8.60 Hz, 2H), 7.53 (d, J = 8.79 Hz, 2H); ¹³C NMR: δ 50.4, 115.8 (d, ³ J_{C-F} = 7.63 Hz), 116.2 (d, ² J_{C-F} = 22.89 Hz), 117.7, 128.5, 129.5, 132.1, 135.6, 140.5 (d, ⁴ J_{C-F} = 2.3 Hz), 157.4 (d, ¹ J_{C-F} = 239.56 Hz); ¹⁹F NMR: δ –124.0 (m).

2.3.18. 2-(4-chlorophenyl)-2-(4-chlorophenylamino)acetonitrile (Table 2, entry 8)

¹H NMR: δ 4.12 (s, 1H), 5.36 (s, 1H), 6.67 (d, J = 8.79 Hz, 2H), 7.21 (d, J = 8.97 Hz, 2H), 7.42 (d, J = 8.61 Hz, 2H), 7.51 (d, J = 8.42 Hz, 2H); ¹³C NMR: δ 49.8, 115.6, 117.7, 125.5, 128.7, 129.60, 129.69, 132.0, 135.8, 143.0.

2.3.19. 2-(4-Bromophenylamino)-2-(4-chlorophenyl) acetonitrile (Table 2, entry 9)

¹H NMR: δ 4.12 (d, J = 8.60 Hz, 1H), 5.37 (d, J = 8.42 Hz, 1H), 6.63 (d, J = 8.97Hz, 2H), 7.35 (d, J = 8.97 Hz, 2H), 7.42 (d, J = 8.61 Hz, 2H), 7.51 (d, J = 8.61 Hz, 2H); ¹³C NMR: δ 49.5, 112.6, 115.9, 117.4, 128.5, 129.6, 131.8, 132.4, 135.7, 143.3.

3. Results and discussion

PVP is well known to form complexes, which have a wide range of uses such as universal surface modifier for immobilization of nano particles, in phase change type liquid crystal device, charge generators in heterolamellar multilayer thin films, in poly(4-vinyl pyridine) electrolytes etc. [5]. Our group has extensively used PVP as an efficient reservoir and carrier with effective release and retaking ability for acids and acid catalysts. Solid PVP-(HF)_n catalysts, developed by Olah and co-workers, have gained use as solid HF equivalents and have been applied as strong, but environmentally safer catalysts for alkylation and fluorination reactions [6]. Much work was carried out on the complexation of the amine compounds, such as trimethylamine, triethylamine, aniline derivatives, etc. with SO2 gas and the properties and behaviour of these solid complexes were well studied [7]. Our group has also explored the synthetic utility of such complexes for many organic transformations [8].

Since cross linked poly(4-vinylpyridine) as mentioned can act as a good solid Lewis base support for acidic reagents, we prepared polymer bound SO₂ complex with poly(4-vinylpyridine) as potential mild acid catalyst for organic synthetic transformations. Recently, Chanda et al. have used PVP-Cu(II) complexes for the oxidation of aqueous SO₂ [9]. However, to our best knowledge, preparation, properties, and use of PVP-SO₂ complex have not been reported in the literature. When we passed SO₂ gas through solid 2% cross linked poly(4-vinyl pyridine) at -78 °C, we observed the formation of a very bright yellow solid fine powder (Scheme 1). From the weight increment, this yellow solid was found to be a 1:1 stoichiometric adduct. SEM studies show that there is no considerable change in the surface morphology of PVP, which indicates the formation of only a coordinated 1:1 PVP-SO₂ complex (Figure 1a and b). Similar information was also obtained when we examined the thermal stability of this complex by TGA. TGA data shows that the complex starts releasing SO_2 at ~ 50 °C (Figure 2) and the release was completed at \sim 130 °C. Therefore PVP can act as an efficient recyclable solid support for SO₂ and the complex can be efficiently used as an SO₂ source.

In order to examine the poteintial of the PVP-SO₂ complex as a catalyst for the Strecker reaction, we first attempted the reaction of 4-chlorobenzaldehyde with

 $Table\ 1$ $PVP\text{-}SO_2\ catalyzed\ \alpha\text{-}aminonitrile\ synthesis\ from\ various\ aldehydes,\ aniline\ and\ TMSCN$

Entry	Aldehyde	Product	Yield(%)
1	СНО	CN NH	86
2	ГСНО	CN NH	94
3	Br	Br H	89
4	H ₃ CO CHO	H ₃ CO H	90
5	CHO CH ₃	CN N CH ₃	86
6	H₃C CHO	CN N H ₃ C	93
7	CHO CF ₃	CN N H	81
8	СНО	H CN	95
9	СНО	CN N	78
10	СНО	CN N H	84

aniline and TMSCN at room temperature using excess amount of the solid PVP-SO₂ complex (500 mg for 1 mmol of substrates). We observed the formation of a mixture of corresponding imine and α -aminonitriles,

under the reaction conditions. We further optimized the reaction conditions (temperature and the amount of PVP-SO₂) and successfully achieved a clean Strecker reaction (Scheme 2) for a variety of aldehydes. The

 $Table\ 2$ $PVP\text{-}SO_2\ catalyzed\ \alpha\text{-}aminonitrile\ synthesis\ from\ various\ amines\ 4\text{-}chlorobenzaldehyde\ and\ TMSCN}$

Entry	Amine	Time(h)	Product	Yield(%)
1	CH ₃ H-NH ₂	1	CI CH ₃ CH ₃ CH ₃	91
2	NH ₂	2	CI H	88
3	NH ₂	2	CI N N	71
4	NH ₂	6	CI H	89
5	Me NH ₂	5	CN Me	97
6	MeO NH ₂	2	CN OMe	98
7	F NH ₂	12	CN F	87
8	CI NH ₂	12	CI N CI	84
9	Br NH ₂	12	CI CN CI CI CN PBr	86

Scheme 1. Preparation of PVP-SO₂ complex.



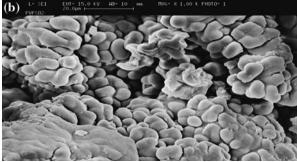


Figure 1. SEM images of (a) PVP and (b) PVP-SO₂ complex.

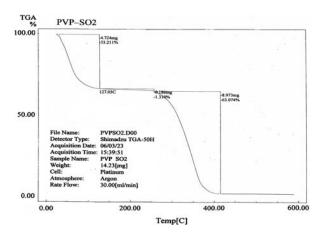


Figure 2. TGA diagram for PVP-SO₂ complex.

results are summarized in Table 1. The amount of PVP-SO₂ used, was reduced from 500 mg to 100 mg to perform the reaction on a 1 mmol scale, but lesser amount of PVP-SO₂ complex (60 mg) was also effective *albeit* under longer reaction time. Simple filtration, removal of the solvent and tituration of the product with excess

Scheme 2. PVP-SO₂ catalyzed three component α-aminonitrile synthesis from various aldehydes, aniline and TMSCN.

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Scheme 3. PVP-SO₂ Catalyzed three component α -aminonitrile Synthesis from various amines, 4-chlorobenzaldehyde and TMSCN.

hexanes afforded the corresponding α -aminonitriles in high yields and purity. No tedious work up or purification process is necessary. PVP can be recovered and recycled. Therefore PVP can be considered as a reversible solid support for SO₂.

We found that aldehydes, bearing electron withdrawing group as well as electron donating group on the aromatic ring, react with almost equal efficiency under similar reaction conditions (Table 1, entry 1–7). Other aldehydes, such as 2-naphthaldehyde, 9-anthraldehyde and cinnamaldehyde also gave clean Strecker products in good yield and purity (Table 1, entry 8, 9 and 10). In the case of cinnamaldehyde, the attack of TMSCN to the internal imine intermediate occurred in a 1,2 fashion, thus leaving the double bond of the cinnamyl group intact in the final product (Table 1, entry 10). However, attempts to perform this reaction with ketones failed. We decided to further explore this methodology by using different amines with 4-chlorobenzaldehyde and TMSCN using PVP-SO₂ as the catalyst (Scheme 3). We found that both aromatic and aliphatic amines provided the corresponding α -aminonitriles in good yields.

We observed significant substituent effects on the rate of the reaction for the amines used. Aliphatic, benzylic and aromatic amines with electron donating groups, react much faster than the aromatic amines bearing electron withdrawing groups on the aromatic ring (Table 2). For example, the reaction of isopropyl amine was completed within an hour and afforded the corresponding aminonitrile in 91% yield (Table 2, entry 1). Similarly, 4-methoxyaniline took two hours to provide the corresponding three component product in 98% yield and high purity. On the other hand, halogenated anilines showed low reactivity towards this three component reaction and took 12 hours for the completeion of the reaction (Table 2, entry 7, 8 and 9).

Majority of these reactions were very clean. Progress of the reaction was monitored by NMR, which shows that the reaction proceeds through the formation of the imine intermediate followed by the addition of cyanide

to provide the final product. Furthermore, the recovered PVP could be recyled to form the PVP-SO₂ complex thus making this method more efficient and useful.

4. Conclusion

In summary, we have prepared solid PVP-SO $_2$ complex and explored it as an efficient, mild and safe catalyst for the one pot three component Strecker reaction of aldehydes, amines and TMSCN to synthesize the corresponding α -aminonitriles in excellent yields and high purity. Readily available starting materials, mild, simple and clean reaction conditions, minimal work up, simple purification and recyling of PVP are some of the salient features of this methodology. Widening the scope of this useful solid catalyst to various other synthetic transformations is currently underway.

Acknowledgments

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